Tuesday, May 12
Facility-specific Workshops

CNM Workshop 4
Exploring the Flatland of 2D Materials for Tribological Manipulation

Location: Bldg. 402, Room E1100/E1200

Organizers: Anirudha Sumant (CNM), Diana Berman (CNM), and Ali Erdemir (Argonne National Laboratory)

The purpose of this workshop is to bring together experts from academia, national labs, and industry to discuss the latest developments in the synthesis, functionalization, and characterization of nanostructured 2D materials, with an emphasis on uncovering their unique tribological properties at the micro/nano-scale and to develop the next generation of energy-efficient moving systems based on the unique wear/friction performance of these 2D materials.

The materials of interest include graphene, boron nitride, molybdenum disulfide, maxenes, and others. With recent fast-paced advances in the development of 2D materials and understanding of their mechanical and tribological properties, we now have a completely new perspective on how they behave as a lubricant compared to traditional thin film or bulk solid lubricants.

The exceptional physical, chemical, mechanical, electrical, and tribological properties of 2D materials, combined with the ability to apply or introduce them on the contacting interfaces of tribological systems, make them ideal new solid lubricant materials for a wide variety of applications, ranging from nano/micro scales (NEMS/MEMS) to macro/meso scales (e.g., moving electrical contacts, sliding/rolling contacts, rotating contacts, bearings, etc.).

The Center for Nanoscale Materials (CNM) at Argonne has expertise and state-of-the-art facilities for the synthesis, functionalization, and characterization of 2D materials. In the last few years the CNM has developed a strong research program in fundamental studies of the physical properties of these materials, with particular emphasis on understanding their tribological properties at the nano, micro, and macro scale.

This workshop will include topics covering fundamental studies on the development of 2D materials and their systematic characterization to understand their structural, surface chemical, mechanical, and tribological properties. It will also cover theoretical and modeling approaches that can provide in-depth understanding of tribo-physical and chemical interactions with the substrate and counterface materials under severe contact pressure and shear stress, issues related to dispersibility, substrate interactions, and possibilities for industrial applications.l

8:30 – 8:45	Anirudha Sumant (Argonne National Laboratory) *Welcome & Introductory Remarks*
8:45 – 9:25	Robert Carpick (University of Pennsylvania) *Mechanisms of Atomic-scale Friction for 2D Materials*
9:25 – 10:05	James Batteas (Texas A&M University) *2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene*
10:05 – 10:35	Break
10:35 – 11:15	Elena Polyakova (Graphene Supermarket Inc.) *The Use of Graphene and Other 2D Materials in 3D Printing*
11:15 – 12:00	Alex Smolyanitsky (National Institute of Standards and Technology) *The Effects of Intrinsic Rippling on the Frictional Properties of Atomically Thin Membranes: A Pathway to Real-time Controllable Surface Properties*
12:00 – 1:30	Lunch
1:30 – 2:10	Yury Gogotsi (Drexel University) *MXenes and MXene-polymer Composites: Manufacturing, Nanoindentation and Nanotribology*
2:10 – 2:50	Christopher Muratore (University of Dayton) *Ultra-thin Transition Metal Dichalcogenides Grown by Physical Vapor Deposition*
2:50 – 3:20	Break
3:20 – 4:00	Nikhil Koratkar (Rensselaer Polytechnic Institute) *Wear in Graphene-polymer Composites*
4:00 – 4:40	Diana Berman (Argonne National Laboratory) *Tapping into Graphene's Potential as a Solid Lubricant*
4:40	Ali Erdemir (Argonne National Laboratory) *Wrap-up and concluding remarks*

WK4

Mechanisms of Atomic-scale Friction for 2D Materials

Robert W. Carpick

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Two-dimensional materials provide a rich playground for exploring new and unexpected physical phenomena, including tribological. This talk will focus on interfacial friction and adhesion behavior of nanoscale contacts with such materials. We find that single layer graphene reduces friction by an order of magnitude for surfaces including copper [1]. However, the friction reduction is layer dependent: for contacts to graphene, MoS_2, $NbSe_2$, and BN, the friction force exhibits a significant dependence on the number of 2-D layers [2] which we attribute to an out-of-plane "puckering" deformation that occurs when the 2-D material is weakly bound to its substrate. However, adhesive behavior does not follow this dependence. Instead, we find that sliding can induce an increased adhesive

force due to local delamination of the topmost layer of graphene [3]. Finally, we observe a large, order-of-magnitude increase in friction that occurs when graphene is fluorinated [4]. This result is interpreted in the context of the Prandtl-Tomlinson model of stick-slip friction, where static friction arises from the high electronic roughness of fluorinated graphene.

[1] Frictional behavior of atomically thin sheets: Hexagonal-shaped graphene islands grown on copper by chemical vapor deposition. P. Egberts, G.H. Han, X.Z. Liu, A.T. Johnson, and R.W. Carpick. *ACS Nano* **8**, 5010–21 (2014). (http://dx.doi.org/10.1021/nn501085g.)

[2] Frictional characteristics of atomically thin sheets. C. Lee, Q. Li, W. Kalb, X.-Z. Liu, H. Berger, R.W. Carpick, and J. Hone. *Science* **328**, 76–80 (2010). (http://dx.doi.org/10.1126/science.1184167.)

[3] Nanoscale adhesive properties of graphene: The effect of sliding history. X.-Z. Liu, Q. Li, P. Egberts, and R.W. Carpick. *Adv. Mat. Interf.* **1**, 1300053 (2014). (http://dx.doi.org/10.1002/admi.201300053.)

[4] Fluorination of graphene enhances friction due to increased corrugation. Li, Q., Liu, X.Z., Kim, S.P., Shenoy, V.B., Sheehan, P.E., Robinson, J.T., and Carpick, R.W. *Nano Letters* **14**, 5212–5217 (2014). (http://dx.doi.org/10.1021/nl502147t.)

WK4

2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene

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Control of friction and wear is a ubiquitous challenge in numerous machined interfaces ranging from biomedical implants, to engines, to nano- and micro-scaled electromechanical systems (MEMS) devices. A key challenge in developing boundary lubrication schemes for such systems is how to reduce wear at the rough surfaces of such devices, where nanoscaled asperities dominate the interfacial contacts. The robust mechanical properties of two-dimensional (2D) nanomaterials, such as graphene, has made it a material of interest for modifying surface frictional properties. While graphene can readily adapt to surface structure on the atomic scale, when deposited on substrates with nanoscopic roughness (~ 10 — 20 nm rms as is common in many machined interfaces) a conformal coating cannot be fully formed due to competition between adhesion to substrate nanoscopic asperities and the bending strain of the graphene. This often leaves a mixture of supported and unsupported regions which respond differently to applied load. Here we describe a combination of AFM nanomechanical and confocal Raman microspectroscopy studies of graphene on silica surfaces with controlled nanoscopic roughness to examine the how this impacts the frictional properties of graphene. Composite interfaces where graphene is supported on self-assembled alkylsilane monolayers will also be described along with the synergistic influence of such mixed interfaces on the frictional properties of the surface.

WK4

The Use of Graphene and Other 2D Materials in 3D Printing

Elena Polyakova

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The 3D printing market is expected to grow quickly over the course of the next few years, without factoring in the likelihood of advances in both printer and filament technologies. One advance is the use of graphene, a 2D material known for its extraordinary attributes, in filament production. Adding graphene to filaments increases the strength and adds conductivity to end-products made via 3D printing — a major advancement when considering using 3D printing for energy storage, electronic, and other commercial applications. I will overview the recent progress made in this area at Graphene 3D Lab, as well as the applications of other 2D materials for 3D printing.

WK4

The Effects of Intrinsic Rippling on the Frictional Properties of Atomically Thin Membranes: A Pathway to Real-time Controllable Surface Properties

Alex Smolyanitsky

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Frictional properties of atomically thin layers and lamellar materials have recently become a topic of significant research interest. As a result, graphene and its chemical derivatives have been suggested as revolutionary solid-state lubricants with unique tribological properties. Possible uses range from novel methods of determining exfoliation energies to nanoelectromechanical (NEMS) applications. Most studies to date have focused on the structural properties, including the effects of chemical modification and substrate interactions.

The first simulated friction force microscopy study of the dependence of the frictional properties of free-standing graphene as a function of temperature is presented. In contrast with the long-standing theory for dry surfaces of solids, sliding friction is predicted to *both increase and decrease* with increasing temperature. The qualitative behavior is demonstrated to depend on the local lateral strains, normal contact force, sample size, and the lateral scanning rate. Our observations are likely due to the intrinsic presence of dynamic flexural ripples in atomically thin layers at finite temperatures. The effect of random thermally excited waves on dry friction suggests the concept of real-time controllable dynamic roughness in free-standing atomically thin layers via imposed lateral strains or externally excited low-energy flexural waves.

The effect of externally engineered rippling content on the frictional properties of free-standing atomically thin layers is described. It is shown that, depending on the excitation amplitude and frequency, sliding friction at identical normal loads can be modified significantly. In addition to possible uses in NEMS applications, the observed real-time control of the effective surface "roughness" may be employed for controllable gas and fluid passage at the nanoscale, as well as for separation of species in gas or fluid mixtures.

WK4

MXenes and MXene-polymer Composites: Manufacturing, Nanoindentation and Nanotribology

Babak Anasori[1], Xin Liu[2], Michel Barsoum[1], Robert W. Carpick[2], and Yury Gogotsi[1]

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Two-dimensional (2D) solids – the thinnest materials available to us – offer unique properties and a potential path to device miniaturization. The most famous example is graphene, which is an atomically thin layer of carbon atoms bonded together in-plane with sp^2 bonds. Recently, an entirely new family of 2D solids – transition metal carbides (Ti_2C, Ti_3C_2, Nb_4C_3, etc.) and carbonitrides – was discovered by our group [1,2]. Selective etching of the A-group element from a MAX phase results in formation of 2D $M_{n+1}X_n$ solids, labeled "MXene." We have produced about 15 different carbides and carbonitrides [2–6]. Their elastic constants along the basal plane are expected to be similar to or even higher than that of the binary carbides. Oxygen or OH terminated MXenes, are hydrophilic, but electrically conductive.

Here we report on manufacturing of Ti_3C_2-PVA composite films [7] and initial studies of their mechanical properties using nanoindentation. At 22±1 GPa, the elastic modulus of the 60 wt.% Ti_3C_2-PVA composite film was measured to be significantly higher than its end members (pure MXene or pure PVA). In addition, tribological properties of different MXenes and effect of the surface termination on friction were studied using atomic force microscopy.

[1] M. Naguib et al., *Advanced Materials* **23** (37), 4207–4331 (2011).

[2] M. Naguib et al., *ACS Nano* **6** (2), 1322–1331 (2012).

[3] O. Mashtalir et al., *Nature Communication* **4**, 1716 (2013).

[4] M. R. Lukatskaya et al., *Science* **341**, 1502–1505 (2103).

[5] M. Naguib et al., *Advanced Materials* **26**, 992–1005 (2014).

[6] M. Ghidiu et al., *Nature* **516**, 78–81 (2014).

[7] Z. Ling et al., *PNAS* **111** (47) 16676–16681 (2014).

WK4

Ultra-thin Transition Metal Dichalcogenides Grown by Physical Vapor Deposition

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Physical vapor deposition (PVD) is a thin film growth technique allowing exquisite control of structure and composition and freedom from many thermodynamic constraints. This is evidenced by the common use of sputter deposition in a significant fraction of the total fabrication steps required to produce ubiquitous commercial electronic devices. By employing well-known theories of film growth and making the necessary conditions a reality through the use of surface engineering technology, thin film microstructures become very tailorable via PVD. This is of particular importance in the field of two dimensional (2D) materials, where processing of continuous and uniform films with thicknesses on the order of 1 nm is currently a major challenge. Transition metal dichalcogenides (TMDs), such as MoS_2 are currently under extensive study as high-performance 2D semiconductors. Using PVD techniques, which are easy to integrate into existing semiconductor device fabrication processes, 2D TMDs can be grown on diverse substrates including SiO_2, graphene, metals, and polymers. This is surprising as it is more common for such thin films to form isolated islands on substrates. Using a variety of *in situ* and conventional *ex situ* materials characterization tools such as Raman spectroscopy and x-ray photoelectron spectroscopy, the mechanisms governing continuous growth of TMDs have been examined for all of the substrates listed above. These substrates possess a broad range of surface energies. It appears that under some conditions a continuous metal monolayer is formed initially on higher surface energy substrates, and normal TMD growth continues on that interfacial metal layer. This is typically observed at high temperature where preferential desorption of the chalcogen atoms during growth is enhanced. How the crystalline domain size within 1–5 nm thick TMD films can be manipulated during PVD growth over at least one order of magnitude, and how the domain boundary density affects electronic, thermal, surface reactivity, and mechanical properties in diverse 2D devices.

WK4

Wear in Graphene-polymer Composites

Nikhil Koratkar

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Polytetrafluoroethylene (PTFE) is one of the most widely used solid lubricants but suffers from a high wear rate which limits its applications. Here we report four orders of magnitude reduction in the steady state wear rate of PTFE due to graphene additives. The wear rate of unfilled PTFE was measured to be ~0.4×10^{-3} mm^3/Nm which is reduced to ~10^{-7} mm^3/Nm by the incorporation of 10 weight % of graphene platelets. We also performed a head-to-head comparison of wear rate with graphene and micro-graphite fillers at the same weight fractions. In general, we find that graphene fillers gave 10 to 30 times lower wear rates than micro-graphite at the same loading fraction. Scanning electron microscopy analysis indicated noticeably smaller wear debris size in the case of graphene/PTFE composites indicating that graphene additives are highly effective in regulating debris formation in PTFE leading to reduced wear. We systematically varied the weight fraction and thickness of the graphene platelets and find that when

the wear results are normalized by the filler specific surface area per unit mass, the results for the various graphene samples fall on a master curve. We use percolation theory to explain these results.

WK4

Tapping into Graphene's Potential as a Solid Lubricant

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In recent years minimizing friction and wear-related failures in mechanical/tribological and electronic subsystems remains as one of the greatest challenges in today's moving mechanical assemblies. It is estimated that nearly 1/3 of the fuel used in automobiles is spent to overcome friction. Accordingly, the search continues for novel materials, coatings, and lubricants (both liquid and solid) that can potentially reduce friction and wear.

In this study we show, that few layers of graphene are able to drastically reduce friction (by factors of 4–5) and wear (by as much as 4 orders of magnitude) of sliding metallic surfaces in both humid and dry environment. This tribological behavior of graphene is strikingly different from its bulk counterpart graphite. Additionally, we observed that the lifetime of such few-layer graphene coating improves significantly, when tested in hydrogen environment [1]. Separate studies on evaluating the electrical contact properties of these graphene sheets demonstrated that graphene, as a two-dimensional material, shears easily during mechanical sliding tests even under high contact pressures, while retaining excellent electrical conductivity of metal-metal contacts for thousands of sliding passes [2]. We elucidate the mechanism of wear/friction of graphene using reactive molecular dynamic simulation. Our findings demonstrate that tuning the atomistic scale chemical interactions holds the promise of realizing extraordinary tribological properties of monolayer graphene coatings.

Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

[1] D. Berman, S. Deshmukh, S. Sankaranarayanan, A. Erdemir, and A.V. Sumant, "Extraordinary macroscale wear resistance of one atom thick graphene layer," *Advanced Functional Materials* **24**, 6640–6646 (2014).

[2] D. Berman, A. Erdemir, and A.V. Sumant, "Graphene as a protective coating and superior lubricant for electrical contacts," *Applied Physics Lett.* **105**, 231907 (2014).